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*Mr. Gourdette*  
*Miss Jones.*

*56*  
UNITED STATES DEPARTMENT OF AGRICULTURE  
*56* Agricultural Research Service,  
Southern Utilization Research and Development Division.

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*2* PROCEEDINGS  
OF  
*2* CONFERENCE OF ADVISERS ON OILSEEDS AND NAVAL STORES, *New Orleans,*  
*1963*

*subject*  
NAVAL STORES STATION  
Olustee, Florida  
April 29, 1963

and

*✓*  
SOUTHERN REGIONAL RESEARCH LABORATORY  
New Orleans, Louisiana  
April 30 and May 1, 1963

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CONTENTS

	<u>Page</u>
Report of Meeting at Naval Stores Station Olustee, Florida, April 29, 1963.....	1
Report of Meeting at Southern Regional Research Laboratory New Orleans, Louisiana, April 30, May 1, 1963.....	10
Report of the Oilseed and Naval Stores Advisers to the Director.....	32
Program.....	38
Attendance List.....	41

APPROVED:



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C. H. Fisher  
Director of Division





CONFERENCE OF ADVISERS  
ON OILSEEDS AND NAVAL STORES

R. M. Persell  
Assistant Director, SU  
General Chairman

Naval Stores Station  
Olustee, Florida  
April 29, 1963

R. V. Lawrence, Chief  
Naval Stores Laboratory  
Presiding

The conference opened at 9:00 a.m. with welcoming remarks by Mr. R. V. Lawrence and R. M. Persell. It was explained that this year's conference had been planned to cover all the formal presentations before lunch in order to leave time for visits to the laboratories and informal discussions with individual scientists. Those in attendance were urged to ask questions or make suggestions at any time during the talks. A special welcome was extended to Mr. George Varn, Varn Trading Co., and Mr. George Williams, Vice-President, Nelio Chemicals, Inc. Mr. Williams is a member of the Forestry Research Advisory Committee.

PINE GUM INVESTIGATIONS

Dr. Walter Schuller opened the technical review. He described a new product from the Naval Stores Laboratory, namely, Photosensitized Oxidized Pine Gum (POPG). This is prepared from the crude pine gum by dissolving in a cheap solvent, adding a trace of a food-type dye, blowing compressed air through the solution, while irradiating with sunlight or any source of visible light. The cost of the product would be about \$0.15-\$0.20/lb. including the pine gum and process costs. The product contains between 0.50 and 0.65 equiv. of peroxide/mole of resin acid present, with the remaining resin acids being non-peroxidic (e.g. dehydroabiatic acid).

Uses are actively being sought at the Naval Stores Laboratory for this new product. Some of the uses under active investigation are to raise the melting point of rosin, to cure styrenated unsaturated polyester copolymeric laminates of the type used in the manufacture of boats, etc., (especially the rosin modified products of this kind under development in these laboratories), hydrogenation to give saturated transannular peroxides which should be useful as vulcanizing agents, and the thermal conversion of the transannular peroxides (and especially their esters) to diepoxides. Diepoxides should have a considerable industrial potential in the plastics field.

DISCUSSION

Discussion of the photosensitized oxidation of pine gum centered around the cost and the catalysts which could be used. Dr. Kadesch was told that the crude product should not cost more than 20 cents per pound to make and the rock-bottom price might be around 15 cents per pound. The pure product from levopimaric acid would cost more and depend on the cost of the pure acid. Dr. Hedrick said this should be 15 to 50 cents





per pound depending how much was being made. Dr. Kadesch asked whether the dye used was critical. Dr. Schuller, Mr. Lawrence, and Mr. Fisher explained that a wide variety of water or alcohol soluble dyes and food colors could be used but that they must have a quinonoid structure like rose bengal or methylene blue. Phthalein dyes won't work. Also, natural chlorophyll which is excellent for terpenes does not work well in this system because of the lack of alcohol solubility.

Later in the discussion Dr. Kadesch asked for clarification of the behavior of neoabietic acid in the photosensitized oxidation. Dr. Schuller explained that in the pine gum oxidation all of the neo gave the diperoxide i.e., both a hydroperoxide group and a transannular peroxide group were added. Dr. Dejarlais asked whether similar diperoxides could be made from levo-pimaric and palustric acids. Dr. Schuller made it clear that neo was unique in this respect and that the hydroperoxide group was formed first.

Dr. Kadesch asked for additional details regarding the use of the peroxides to raise the melting point. Dr. Schuller stressed that this work was in an early stage of development and that a range of temperatures and peroxide concentration in the range of 1 to 5 percent were being tried. Mr. Minor said that about twice as much increase in melting point (22 degrees) had been obtained with the peroxide as is obtained by just heat-treating rosin. In response to questions by Drs. Enos and Harwood, he gave 175°C. for 4 to 5 hours as the best conditions found so far. Higher temperatures were suspected of decomposing the peroxide too rapidly to get maximum effect as a catalyst.

Dr. Enos asked whether a promoter such as cobalt was used with the pine gum peroxides to cure polyester resins. When told that it was not he asked what temperature was used. Mr. Halbrook said this was done at about 130°C. Dr. Enos stressed that if it was to be used for boats or other large objects it would have to work at about room temperature, and that it generally required peroxides which worked well with promoters, as very many do. Dr. Kadesch mentioned that percarbonates, and the like, which decompose at room temperature were also used. Dr. Schuller agreed that further tests should be made using promoted systems at room temperature. Dr. Enos asked whether the half life of the peroxides had been determined and was told that they had not but that a 25% solution of the pine gum peroxide in toluene lost 35% of its active oxygen in 6 hours at 110°C. but that the ester decomposed more slowly. Dr. Enos asked about the method used to follow the disappearance of peroxide since they had experienced interference by the double bond in terpene peroxides. Dr. Schuller said that although the stoichiometric values were not obtained the aqueous KI - chloroform - acetic acid method used gave consistent values and in the case of the peroxy acids gave almost zero values at the end of the decomposition reaction.

Dr. Kadesch mentioned that the chemistry of ascaridole should provide a good guide to the reactions to be expected from LAPO. Dr. Schuller agreed with this in general but thought the acid group might affect the decomposition. (For further comments on this point see discussion of use of pine gum peroxides for vulcanization.)





With regard to the isomerization of the levopimaric acid photoperoxide (LAPO) to a diepoxide, Dr. Enos asked if only the acid had been used. Dr. Schuller said no but that anomalous peroxide contents were obtained with the ester, rotation changes occurred on heating but there was no change in apparent peroxide content. He suggested that the diepoxide might react with HI to liberate iodine, and indicated a possible mechanism in response to a question by Dr. DeJarlais. Dr. Kadesch asked about determination of epoxide content in the products. When Dr. Schuller said he had not done this but planned to do so with an HCl method, Dr. Kadesch recommended checking the tentative method using commercial HBr which had just been adopted by AOCS. Dr. Kadesch urged the use of esters rather than acids in the initial studies to avoid destruction of epoxide by acid. Dr. DeJarlais asked whether polymeric decomposition products were obtained. Dr. Schuller said he suspected they were but hadn't proved it yet.

Dr. Schuller requested any suggestions as to why he should get a conjugated diene during reduction of the peroxide in addition to the expected diol but none were received.

The suggestion that the photosensitized oxidate of pine gum be used as a vulcanizing agent led to considerable discussion. Dr. Enos stated that they had tried it for GRS and for ethylene-propylene rubber and even for polyethylene or propylene and got no vulcanization and very little evidence of free radical decomposition. In response to a question by Dr. Schuller, he said that catalysts which were active for vinyl polymerization were not necessarily vulcanizers. Large concentrations e.g. 2% of peroxide are required for vulcanizing in contrast to 0.1% or less for some polymerization. Traces of hydroperoxide even in the "pure" transannular peroxides could be responsible for their activity in polymerizing polyesters. In view of Dr. Schuller's earlier comments about acid catalyzed decomposition, he now felt that this could have been responsible for the failure of the acid peroxides to vulcanize. Dr. Enos stated that ascaridol is not effective as a vulcanizer but the saturated ascaridole is. It was concluded that the saturated resin acid peroxides would probably be vulcanizing agents and that the unsaturated resin acid peroxides on heating were going over to epoxides and not free radicals. Dr. Enos stated that the potential outlet for such products was in ethylene-propylene rubbers (EPR) and that industry was apparently not going to make these but instead would make ethylene-propylene-diene terpolymers (EPT) which could be vulcanized with sulfur similar to conventional rubbers. Dr. Schuller said that in view of our inability to prepare saturated peroxides we had already decided to emphasize the production and use of the diepoxide rather than the production of a vulcanizer. Dr. Kadesch expressed the opinion that the best chance for a large scale use would be one in which the unique resin acid structure was advantageous.

Mr. N. J. Halbrook reported the results obtained in preparing polymerized polyester resins from the adducts of rosin and  $\beta$ -propiolactone. He described the conditions used in preparing the adducts and the polyesters and presented the results of the evaluation of their copolymers with styrene.





The end products were fully comparable to commercial products and superior in some respects. He further reported that by using a high temperature preesterification technique the  $\beta$ -propiolactone required could be drastically reduced or perhaps even omitted. Preprints of a paper covering this work were distributed.

## DISCUSSION

Dr. Kadesch asked how we explained the relatively good results with unmodified rosin i.e. no  $\beta$ -propiolactone. Mr. Halbrook and Mr. Lawrence said that dimerization during esterification was the major factor as indicated by reduction of conjugation in the glycol-rosin ester. Condensation of the remaining 5 or 6 percent of abietic-type acids with fumaric acid was also possible. The possibility of reaction of mono-enes with fumaric to give substituted succinic acids was also mentioned. In response to a question Mr. Halbrook said that some work using maleic anhydride had been done and that more was planned.

Dr. Kadesch asked why acrylic acid (as reported in a German patent) gave different products than  $\beta$ -propiolactone. Mr. Halbrook explained that the patent in question did not give enough details to tell for sure but polymerization of the acrylic acid was undoubtedly a factor.  $\beta$ -Propiolactone breaks down slowly so there is never much acrylic acid present. Differences in the esterification step could also be involved.

Dr. Kadesch asked about the structure of the  $\beta$ -propiolactone modified rosin - whether there was a preferred orientation. Mr. Halbrook replied that there was some and that two of the isomeric adducts had been isolated and their structures pretty well established. These account for 70 percent or so of the product. Both other isomers are probably present but they have not been purified yet. He also asked whether the two carboxyls in the adduct had the same reactivity. Mr. Lawrence said he thought the one from the  $\beta$ -propiolactone was a little more reactive than the one from rosin. In response to a question by Dr. Enos, Mr. Halbrook said that it took about an hour at 225°C. to prepare the rosin- $\beta$ -propiolactone adduct. Foaming and reflux limit the rate of addition of the lactone. Dr. Kadesch asked whether we would expect a different product ratio with acrylic acid and whether the acid would react at a lower temperature. Mr. Lawrence said the distribution of isomers might be different but he didn't believe the acid would add at a lower temperature.

In closing, Mr. Halbrook described the different tetracyanoethylene adducts of the abietic-type acids. Dr. Kadesch asked why most of the adducts failed to show  $C\equiv N$  absorption and was told that this was characteristic of gem-cyano groups. The general behavior of the abietic-type acids with dienophiles was discussed and Mr. Fisher pointed out that TCNE was unique in that it reacted at room temperature with all isomers and gave a separate product for each. The usual dienophiles require such high temperatures with the acids other than levo that they all give the levo adduct.





Mr. N. M. Joye, Jr. discussed the unidentified portions of rosin and pine gum with emphasis on the acids. Eight resin acids have been isolated from American pine gum or rosin. Mr. Joye described the isolation of a new one and showed that it corresponded to an alcohol previously isolated. This is the first bicyclic resin acid from this source. The acid and alcohol each occur in slash rosin to the extent of 5%.

## DISCUSSION

Dr. Kadesch asked how many more resin acids might be present in rosin. Mr. Joye said at least 6 or 8. Three have been isolated in small quantities and doubtful purity. The unidentified acids probably occur in concentration of less than 2% each. It was pointed out that slash gum had a more complex composition than longleaf and that our efforts had been concentrated on slash because of its greater economic importance. It was pointed out that the minor acids may contribute more than their share to the properties of the rosin.

## Rosin Investigations

Dr. G. W. Hedrick described recent research which has disclosed that gum rosin size can be made more efficient by removing the neutral materials from it. Several processes for accomplishing this were described. He also described work on making isocyanates from resin acids and on the reactions of levopimaric acid with sodium hypohalites. An outline describing this work together with various reactions of pinonic acid,  $\alpha$ -pinene epoxide and related compounds was distributed and these reactions were discussed in some detail. Research on production of monomers for testing under a contract with C. S. Marvel was also outlined.

In connection with S. C. Johnson Co's. interest in the production of diphenolic compounds from pinonic acid, Dr. Kadesch asked whether it was possible to keep the cyclobutane ring intact or whether the lactone was always obtained. He was told that the lactone was always obtained.

Dr. Enos asked whether the acetylenic compound from pinonic acid or any of the others had been sent to Beltsville for testing for herbicidal activity. He said they had screened perhaps 100 acetylenic compounds and that they were amazingly active. Many showed selective herbicidal action. Dr. Hedrick indicated that our past experience with the length of time it took to get any results back had discouraged us from sending additional samples.

Dr. Schuller asked whether epoxides like  $\alpha$ -pinene epoxide i.e. ones from tertiary olefins were generally unreactive in polyether formation. Dr. Kadesch replied that he didn't think any generalization was very safe. It depended on other steric effects, the catalyst used etc. However, there is usually a preference for formation of the tertiary alcohol when the epoxide ring opens and such alcohols tend to dehydrate and stop the polymerization. He then asked whether the zinc bromide rearrangement of the epoxide had a name and whether it was a general reaction. Dr. Hedrick said he didn't know any name for it and that optical activity had no effect on the reaction.





Care with which the zinc bromide was prepared and the way it was used was critical. In reply to a further question he said mineral acids or even other Lewis acids did not give the same results. Mr. Fisher stated that the reaction was probably a very specific one involving an intermediate complex which underwent a series of rearrangements and that the cyclobutane ring was a necessary part of the reaction.

Dr. Enos suggested that the glycols such as those from pinic and homopinic acid be used to make phosphorous derivatives using techniques developed for cotton at SU and that these then be used for foamed in place fire resistant polyurethanes. Potential market in this area is very large. Insulation of ships' hulls is a particularly promising use.

In connection with the dimethyloctadienes, Dr. Enos asked how easy it was to separate the two isomers. Dr. Hedrick indicated that this was a problem and that only the 2,4 dimethyl one gave good polymers. In response to a comment by Dr. Schuller, Dr. Kadesch pointed out that EPR polymerizations occurred on a catalyst surface and that the branching on the 2-carbon atom could have a marked effect on the ability of the olefin to fit onto this surface.

Mr. H. B. Summers described the large scale process which has been developed for separating levopimaric acid of any desired purity from pine gum. In response to questions by Dr. Reaville, Mr. Summers pointed out the flexibility of the method, and clarified the method of recovering the residual rosin from unreacted pine gum. Mr. Summers also described a unique combination of gas chromatography and acid isomerization used to determine the composition of the mixtures obtained at various stages in the process. In response to a question by Dr. DeJarlais, he agreed that longer columns might be used to advantage to improve the resolution of the various methyl esters. When questioned about the presence of levopimaric acid in a rosin sample, Mr. Summers explained that this was a laboratory sample which had not been heated as severely as commercial samples.

Dr. B. A. Parkin discussed the reaction of formaldehyde with rosin, resin acid mixtures and pure resin acids. He pointed out that the goal of the work was to get diols - one OH by addition of a methylol group, the other by reduction of the acid group of rosin. For this the neutrals present in rosin are undesirable. Methods of getting resin acid mixtures high in abietic-type acids were discussed and it was reported that such mixtures did not react nearly as well with formaldehyde at 130° as the rosin itself did. When pure levopimaric acid was tried, a rapid reaction occurred but the crystalline product obtained had no OH group and no UV absorption. On heating further, a resinous hydroxy compound was obtained.

Dr. Kadesch asked how much formaldehyde was incorporated in the resin acid mixtures. Dr. Parkin said that the usual active hydrogen determination with lithium aluminum hydride indicated from 0.5 to 1.0 moles per mole of resin acid. Rosin adds one mole per mole. The abnormal behavior of levopimaric acid contributes to the difficulties of determining the extent of





addition. Dr. DeJarlais suggested that a pyran might be obtained from levo by a sort of Diels-Alder addition. He asked whether U.V. absorption reappeared on heating the crystalline adduct and was told that it did to some extent. In response to a question by Dr. Kadesch, Dr. DeJarlais said his "Diels-Alder" suggestion was purely speculative.

Dr. Reaville asked whether the acid number remained constant and Dr. Parkin told him it decreased some, probably because of ester formation. Dr. Kadesch asked about the solubility of formaldehyde in these reactions and was told that it dissolves pretty well in rosin or perhaps just reacts quickly. Apparently paraformaldehyde must break down before it dissolves and reacts. Dr. Kadesch asked whether formaldehyde modified rosins were being made commercially and was told that they were. Mr. DeJarlais asked about the reaction of resin acid esters and was told they did not react at all well with formaldehyde. This suggests that the reaction is catalyzed by the resin acid.

#### TURPENTINE INVESTIGATIONS

In order to complete the formal presentations before lunch, the review of the work in turpentine investigations was kept very brief. Mr. G. S. Fisher brought the group up to date on the cooperative work with Forest Service on analysis of pine gum from individual trees. Relative constancy of turpentine composition from year to year was observed. Nature of the root stock did not affect the turpentine composition of gum from the shoots of grafted pines. Loblolly pines which survived in stands which had suffered massive attack by southern pine beetle produced turpentine containing more alpha-pinene than average trees from stands nearby. Mr. Varn expressed considerable interest in this work and suggested rather facetiously that maybe they should try spraying their trees with turpentine instead of BHC for black turpentine beetle. (A recent Southern Forest Experiment Station publication actually reports that when turpentine is used as the solvent for BHC, the beetles are attracted to the sprayed trees.)

Dr. Schuller asked how accurate the analyses were and he was told that for major peaks they were probably accurate to  $\pm 2$  or 3 percent of the amount present. About 0.5 to 1% is the minimum amount that can be detected in the standard analysis. With special care greater accuracy and lower limits can be achieved.

Mr. R. L. Kenney outlined briefly research on acid isomerization and disproportionation of terpenes and on the production of conjugated p-menthadienols by photosensitized oxidation followed by base-catalyzed isomerization. Dr. Kadesch and Dr. Schuller asked for and received additional details about the isomerization. Dr. Enos stated that they had also encountered the inability to get gamma-terpinene to isomerize completely to alpha-terpinene which Mr. Kenney had noted. It was agreed that one should be very cautious about extending rules based on acyclic compounds to cyclic ones.



Mr. George Williams said he had some suggestions to pass on to the group. Copies of these were made and distributed. In particular, he recommended additional work on methods of analysis for all types of naval stores products. The research staff of his company contacts the Laboratory frequently for assistance on analytical problems.

The afternoon was devoted to visits by the advisers in small groups to the various laboratories where the scientists showed them samples of new products and answered any additional questions.





The following suggestions were made by Mr. George Williams,  
Member of the Forestry Research Advisory Committee

One of the more important areas in which Olustee could be of general benefit to the industry is in the analytical area especially gas chromatography. This would help especially if they could set up standard procedures for determining the commonly occurring terpenes in standard products such as the turpentine and commercial derivatives thereof. This should include the determination of other compounds also such as methyl chavicol and anethole.

Another broad problem helpful to the industry would be the upgrading of lower grades of rosin to higher grades - probably starting with the oleoresin.

It would also be quite helpful if Olustee would incorporate all the published work done there into a book. That is an indexed collection of reprints.

It would also be helpful if the industry had a booklet including physical data on terpenes. A collection of infrared and ultraviolet data could be included. This data could be included in a booklet with gas chromatography analytical data.

Phenol coefficients of various pure terpene alcohols and ethers.

If the above analytical information can be obtained, it will be necessary to prepare pure samples of the various materials. Enough of each pure sample should be obtained to be able to distribute samples to industry laboratories where they could be used in their own analytical work. This would be quite valuable.

A study of the structures of the coloring matter in rosin. Find out something about the nature of such material.





Southern Regional Research Laboratory  
New Orleans, Louisiana  
April 30 - May 1, 1963

R. M. Persell  
Assistant Director, SU  
Presiding

Attending the meeting in New Orleans were Dr. DeJarlais, Dr. Enos, Dr. Harwood, and Dr. Kadesch. Dr. McBee joined the group later. Following a welcome by Dr. Fisher, Dr. Goldblatt, who had recently been appointed Chief of the Oilseed Crops Laboratory, presented a general view of the research program on Oilseeds. This was followed by discussions of current research in the following areas: confectioners' fats, new polyester fats, cyclopropene fatty acids, fatty amide derivatives, fire-retardant coatings using tung oil alkyds, new crop oils, fat emulsions for intravenous alimentation, and related oilseed and vegetable oil topics. Last years' recommendations were reviewed and the action taken made known to the Advisors.

Dr. Fisher's remarks: "We are very glad you are here. I want to extend our greetings to our friends of industry and of the Northern Laboratory. I regret I couldn't be with you at Olustee. I am sorry our Southern transportation delayed your arrival time, but you arrived safely and that is the most important thing. Among events of the past year was the appointment of Dr. Leo A. Goldblatt as Chief of our Oilseed Crops Laboratory. Dr. Goldblatt was a member of the Oilseed Crops Laboratory here before he went to our Western Division and you may have met him here before. He has an excellent reputation in the field of fats' and oils' chemistry.

Another important event of the past year has been with a useful commodity that will be very helpful to us, that is, money. We had not had a substantial increase in the past years and this nice increase in the past year will be very helpful and will allow us to expand our research. We are looking for good men, but the supply of good men is limited. I'm not asking you to directly recruit for us, but if you know of any well qualified men we will appreciate your telling them about our laboratory openings and positions and ask them to contact us. I will be glad to answer any questions about available positions.

We appreciate your taking time from your busy schedules to visit us, and are looking forward to discussing our oilseed research with you."

Dr. Goldblatt's remarks: First, I would like to take this opportunity of joining Dr. Fisher in welcoming you and I hope our association continues for a long time. I must confess in the presence of my boss that I don't know everything yet about all the work going on in the Oilseed Crops Laboratory but hope to acquaint myself closely with all the work as soon as possible. I have noticed in the "brown book" prepared for you that it makes mention of naval stores and oilseeds, in particular, oils of the oilseeds, and no mention was made of meals. The interest in oils is in keeping with organic chemistry, but the oilseed meals cannot be neglected from the point of view of economics. For example, in the case of soybeans the meal accounts for about 55% of the value, and the oil accounts for only 45%. Of course, this higher value of meal over that of the accompanying oil is not necessarily the case with all





the other oilseed products used commercially. I asked Frank Dollear to make a survey for me of the Oilseed Laboratory here, and he reported that about 3/4 of our research effort is devoted to oil and slightly less than 1/4 to meal. We work mainly with 3 major oilseeds, cottonseed, peanuts, and tung. A small amount of our time is spent studying new crops and their potential products. The new crops (oilseeds) investigated are: Cuphea, Limnanthes and certain Umbelliferae, as part of the work on sources of unusual fatty acids. We are also engaged in a study of confectionery fats. We have a contract with Dr. Marvel who is studying polymerization of various monomers derived from our materials.....; a contract with Dr. Shirley of University of Tennessee who is studying the chemistry of gossypol; one with Dr. Rinehart of University of Illinois who is doing research on cyclopropenoid acids. We have just begun a new contract with Evans Research and Development Corporation, who will be studying the flavors and aromas in processed peanuts. At the same time while we are supporting research at other institutions, certain groups support research in our organization. For example, the National Cottonseed Products Association is supporting a project here on pigmentation of cottonseed oil; another group, the Foundation for Cotton Research and Education, supports work here on cyclopropenoid acid of cottonseed oil. The National Confectioners Association is supporting research in our laboratory as well as the Pan American Tung Research and Development League. The Army is assisting in financing two studies here: (1) fat emulsions for intravenous injection; and (2) work on fire-retardant protective coatings. We are also involved in the Public Law 480 Fund program: In England there is a project to study the glyceride distribution in cottonseed oil. Another group in France is studying aryl alkyl ketones and derived products from fats. We are supporting research in Uruguay on derivatives of gossypol and finding uses for them. In India there are 4 different projects being carried out. One is at Bombay with a group studying physical properties of triglycerides; another at Bangalore is working on addition of carbenes. In Poona there are two projects: one is for work on tung oil and another on glycol ethers.

Please feel free at any time during the discussions to ask any questions and make any comments you wish. Several of our projects were completed recently; several others are to be discontinued shortly. We have to consider what areas of work need to be strengthened and which can be de-emphasized. This can be done when we prepare new line projects. We welcome all your suggestions and comments. I don't promise to take all of your comments and suggestions but I do promise to consider each of them very seriously in making up our program of work.

#### REVIEW OF RESEARCH ON CONFECTIONERS' FATS

A review of the research on confectioners' fats was given by Mr. Norman V. Lovegren. The objective of this research is to develop techniques for converting cottonseed and peanut oils and their derivatives into useful cocoa butter-like fats and specialty confectionery fats and oils, especially those that are currently unavailable or are being made from coconut and other foreign oils.





## DISCUSSION

Dr. Kadesch asked, did you start with a monoolein? Mr. Lovegren replied, yes, essentially. Dr. Kadesch said, you say the desired mixture; do you mean as to configuration? Do you mean the 1-oleostearic? Mr. Lovegren replied, yes, the desired material is an oleo-di-saturated material.

Dr. Kadesch asked what were the properties of the 70% yield material referred to. Do you know the relative amounts of the 1- and the 2-position material (oleoyl)? Mr. Lovegren replied that in the best product obtained of the oleo-disaturated material about 2/3 of the oleic was in the one position and about 1/3 in the two position.

Mr. Feuge observed, perhaps someone can tell us how to make a 50-50 mixture from the diglyceride of oleic and stearic esterified with stearic acid. Dr. Kadesch asked have you attempted synthesis for making the 2-oleo-distearate by special procedures to put it in the 2 position? I think the synthetic route could be tried to provide you with the material you need. Mr. Feuge replied we have done a lot of work on the synthesis of polymers from diglycerides. We know how to make the material synthetically. But this would be on a laboratory scale and we know that the laboratory scale procedures are not practical for a commercial basis.

Dr. Kadesch asked, did the synthesized material behave like cocoa butter? Mr. Lovegren replied, yes, we made a mixture of the two major components of cocoa butter: 2-oleodistearin and 2-oleopalmitostearin. The physical properties of the mixture were the same as those of cocoa butter. With oleic in the end or in the middle position you get two different X-ray diffraction patterns. In a synthesis where we tried to make 2-oleodistearin by esterification of 1,3-distearin with oleic acid, the X-ray pattern of the product showed both 1-oleo- and 2-oleo-distearin present, and the ratio was about two parts of 1-oleodistearin to one part of 2-oleodistearin. This was based on X-ray data before and after esterification. I realize the accuracy of the X-ray method for making such a conclusion is not too good, but that was the tool we used to arrive at this conclusion.

Dr. Kadesch asked, have you considered the acyl glycidyl ester approach for the preparation of 2-oleo- products or is that too expensive? Mr. Feuge replied, no, we need to have the oleostearin and the dipalmitin. We have looked at epichlorohydrin. Benzylglycerol is another one. Dr. Kadesch observed, then, if you can get the 1,3-position, by reaction with acyl chloride, from then on it will be easy to make the 2-oleyl products. Mr. Lovgren noted, you will not run into rearrangement problems there. Mr. Feuge noted that we had a lot of trouble making the diglyceride. It is a slower process and does furnish much rearrangement. In response to a question, Mr. Lovgren replied we did not consider ring opening of the glycidyl ester to give directed opening as a method for making the 1,3-diglyceride? When asked if the fatty acid and the glycidyl ester would give the 1,3-glyceride, Mr. Feuge replied that it will rearrange. About 50% will go the 1,2-position.

Dr. Kadesch asked if that was done at relatively high temperature?

Mr. Feuge replied, yes, and the process was speeded up by presence of the acid catalyst.





Dr. Kadesch noted that ring opening under acid or alkaline conditions can be done at milder conditions than the conditions used for esterification. Mr. Lovegren asked, what are you thinking about there to give the triglyceride? Dr. Kadesch said I was thinking about using the acid chloride, of reacting the 1-3-diglyceride with oleoyl chloride. This may give the oleic in the 2-position. Of course, shifting may be a problem there. Mr. Feuge said that we have studied the Schotten-Baumann reaction (using acyl chloride.)

The question of economics to consider in the use of this material commercially arose. Mr. Feuge stated that we are competing with cocoa butter that is selling for \$0.60 to \$0.65 per pound and with other fats selling for \$0.20 per pound. Dr. Harwood asked if it would still have the flavor of cocoa butter. Mr. Feuge said that that is a matter of conjecture. Grinding or conching and presence of some chocolate liquor add to the flavor. Mr. Dolllear stated that the product can't be called chocolate unless it contains cocoa butter.

#### REVIEW OF RESEARCH ON NEW POLYESTER FATS

A review of research on new polyester fats was given by Miss Audrey T. Gros. The objective of this research is to prepare from cottonseed oil new-type polyesters, including polymers, which are specifically designed to provide special new-type fat products for food and other industries, and to characterize and evaluate these new-type products.

#### DISCUSSION

When asked by Dr. Kadesch if she had said that the monooleostearin was 90% material, Miss Gros replied that it was 99% plus purity. The starting products were pure material.

Dr. Kadesch noted that we know from the literature that alkaline conditions give a random distribution, and that with acid condition you can get some direction of reaction. Mr. Feuge stated that our reaction will not go without a catalyst unless there is some water present.

Dr. Kadesch asked, then you're getting self catalysis by the acid? Mr. Feuge replied, we get catalytic action with acetic acid. Dr. Kadesch noted, it is common practice industrially to make triglycerides without any catalyst. And there is no breakdown in the products as far as I know. Do you think the monoglycerides could be made without a catalyst by using higher temperature? Mr. Lovegren stated, I think you are speaking about interesterification conditions. Dr. Kadesch replied, yes, I suppose you would get some there. Mr. Feuge asked, what temperatures? Dr. Kadesch replied, the temperatures are between 200 and 300°. Mr. Feuge stated that we use a temperature under 240°. At 240° breakdown and rearrangements occur. Mr. Lovegren said, at 210° we didn't get much rearrangement.

Dr. DeJarlais asked, how does the rate of alcoholysis of an ester (acid catalyzed) compare to the rate of esterification of an ester? (Reaction of an alcohol group with an ester vs. monoglyceride with an acid.) Mr. Lovegren





asked, you're taking out the water? Dr. DeJarlais replied, this wouldn't involve water. Mr. Feuge said, interesterification is another thing. We are talking about esterification in our procedure. The diglycerides formed in the presence of the acid catalyst are fairly stable. On the other hand, very stable triglycerides can be produced under anhydrous conditions with p-toluenesulfonic acid catalyst. Dr. DeJarlais asked, then, the water is involved in your reaction? Mr. Feuge replied, there are published papers telling about the use of anhydrous condition in work with blood plasma. If we use anhydrous conditions, we get the product we want. There is interesterification if water is present in the esterification of diglycerides. If conditions are random, you can calculate what you get. Dr. Kadesch said that it would be to your advantage to be able to start at higher temperatures and without a catalyst. This would eliminate the removal of catalyst upon completion of the reaction, if the reaction could be carried out without a catalyst. Mr. Feuge replied, these reactions are carried out at 80° or 100° C. Without a catalyst high temperatures are necessary and rearrangements take place. We need the catalyst.

Dr. Kadesch asked, have you tried the reaction of amylose in acetonitrile with the methyl ester in the presence of potassium tertiary butoxide as a catalyst in the Snell process? Miss Gros replied, with the Snell procedure, we used potassium carbonate, and the solvent was dimethylsulfoxide.

Dr. Kadesch asked, when you used the Snell process, did you do it at the boiling point of the solvent? Miss Gros replied, dimethylsulfoxide boils at 180°; we carried out the reaction below the boiling point of the solvent. Dr. Kadesch observed, sometimes dimethylsulfoxide breaks down at its boiling point. There are solvents of a similar nature which can be used, and this breakdown can be avoided. Miss Gros replied, we have tried dimethyl formamide. Dr. Kadesch suggested the use of tetramethylenesulfone which has a boiling point of about 220°. It is more stable than dimethylsulfoxide and has a real advantage over DMSO. Miss Gros replied, perhaps we can do more work on the Snell process using tetramethylenesulfone. Dr. Kadesch stated, I would seriously suggest the use of the higher boiling solvent for this type of work.

Dr. Goldblatt asked, how do they make lactopalmitins industrially? Dr. Kadesch said, perhaps someone here knows how that is done today. Dr. Harwood replied, it is by a simple base catalyzed esterification of lactic acid with common monoglyceride of commerce. Dr. Goldblatt asked, there is no solubility problem there? Dr. Harwood replied, no, all the "gemisch" is solubilized.

Dr. Kadesch asked, hasn't the antifungal activity of medium chain length fatty acid been known for a long time? Miss Gros replied, yes, but we are talking about triglycerides. Dr. Kadesch asked, but couldn't they be serving as just a source of fatty acid? It seems that there is a lot of literature from which to draw these facts. Mr. Holmes stated, we have made a very extensive literature survey of the antifungal activity of fatty acids, of capric acid and lots of other ones. Many of these acid derivatives are reported to have such activity. Dr. Kadesch stated, with the ozonides of glycerides, it has been found that the active principle for antifungal activity was the pelargonic acid that came from breakdown of the glyceride. Miss Mayne





said, we are using the triglyceride because it offers a source or pool of activity which can be slowly broken down and would furnish longer lasting activity than by simply adding a fatty acid to a commercial product such as bread. Mr. Feuge added, yes, the purpose is to get a material which will slowly break down to furnish a continuing antifungal activity. Dr. Kadesch stated that a pharmaceutical house might be attracted to testing these materials as an antibacterial agent against the tubercular bacillus, particularly because of the potential use of the fatty acid against the tubercular bacillus.

#### REVIEW OF RESEARCH ON CYCLOPROPENE FATTY ACIDS IN COTTONSEED OIL - ISOLATION AND IDENTIFICATION

Mr. R. O. Feuge reviewed studies on the isolation and identification of cyclopropene acids in cottonseed. These studies are part of a project to protect and increase the utilization of cottonseed products by developing (1) information on the chemical and physical properties of cyclopropene acids, (2) improved or new methods for analysis for these acids, (3) means of converting cyclopropene acids constituents into physiologically inactive derivatives, (4) information on the influence of conventionally modified and new methods of processing cottonseed and cottonseed products on the reduction of cyclopropene acids.

#### DISCUSSION

Dr. Kadesch asked, is malvalic acid the same as sterculic? Mr. Feuge replied, the C19 acid is sterculic acid; the C18 acid is malvalic. The cyclopropene ring is at 9-10 in sterculic and 8-9 in malvalic. Dr. Kadesch said that malvalic is then one carbon atom less, and the cyclopropene ring is one carbon closer to the carboxyl. He asked, did you say there was 0.4% malvalic acid in cottonseed oil. Mr. Feuge replied, that is an average value. Some commercial oils are negative and Dr. Skau has found some to contain an average of about 0.6%. Dr. Kadesch said, you said that hydrogenation can knock out the malvalic acid. How about oxidation? Mr. Feuge replied, the addition of citric acid and reaction under deodorizing conditions will destroy much of the cyclopropene ring, so I would say oxidation can affect it as well as hydrogenation. The dibasic acids seem best for the acid treatment if used at the right temperature and conditions. Citric acid for 15 minutes at 180° will destroy all the cyclopropene acid. It makes a polymer with S. foetida oil. Dr. Kadesch said, as I understand it, you can open the ring half-way or all the way. What are the products of the half-way reaction. Mr. Feuge replied, we have proof of at least 3 products. The methyl seems to be present in about equal quantities. Hydrogenation destroys the double bond.

Dr. Goldblatt asked, what conditions did you use, Reuben, for the results shown on that slide? Mr. Feuge replied, thirty minutes at 160° C. under anhydrous conditions. Dr. Goldblatt requested, Reuben, tell us the concentration ratio.

Mr. Feuge responded, each reagent was present at a level of 0.012 mole per 100 g. of oil. The 100 g. of oil contained about 0.012 mole of cyclopropene.

Dr. Kadesch asked, was all done in anhydrous conditions? Or did you use aqueous medium? Mr. Feuge replied, anhydrous conditions were used.

Dr. Kadesch asked, what temperature did you say? Mr. Feuge replied, 160°.





Dr. Kadesch said, I know about the observed effect of the cyclopropene oils on egg color, but I don't know of any suggestive evidence of harmfulness of cottonseed oils to humans. Why go to all the trouble of finding ways to destroy this acid, if you don't know whether it has any harmful effects on humans. Mr. Feuge replied, we were put under a crash program. We had to find out ways to get rid of the cyclopropene acid because of the interest by the cottonseed processors and our laboratory. Dr. Frampton will be telling you later about the physiological effects of the acid. Mr. Hoffpauir said quite the contrary, cottonseed oil has been used as a food by humans for many years without any record of ill effects. The interest in the malvalic acid arose from the observation that it was the material which was causing the increased permeability of the vitellin membrane of the hen egg. There has been a study on the changes in the ratio of oleic to stearic acids in animals fed oils containing malvalic acid. However, I will say that this work on cyclopropene acids is allowing us to learn some interesting chemistry about these acids now that we have been given the opportunity to do so. Also, we would like the information should objections to cyclopropene acids in foods become an issue.

Dr. Kadesch stated, you mentioned doubting of double bond shifting. Is the conclusion from this that there is no isolated trans bond? Mr. Feuge replied, yes, this is based on one run only. There was no trans as indicated by the absence of a band at the  $10.3 \mu$  in the IR spectrum. Dr. Kadesch said, if you could go one step further and shift the double bond to conjugation with ring, and this may not show a trans band in the IR; neither structure shows typical ring? Mr. Feuge replied, it was never found. Neither one showed it. Dr. Kadesch asked, is the double bond in the ring a cis or trans bond? Mr. Feuge replied, I don't know. Dr. Kadesch asked, is the cyclopropene acid ring more susceptible to oxidation than oleic? Mr. Feuge replied, Yes. Dr. Kadesch observed, this seems reasonable on basis of allylic configuration from structure.

Dr. Harwood asked, is synthesis an unreasonable means of obtaining the pure materials? Mr. Feuge replied, probably so, they are very reactive. We tried fractional distillation. It is about as close as trying to separate linoleic and oleic on a distillation column. It is that close. Mr. Dollear remarked, the material is heat sensitive. Dr. Kadesch asked, what about high vacuum distillation? This could be done at lower temperature. Dr. Goldblatt observed, I suppose that could be tried at about 30 microns. Dr. Harwood asked the melting points of the acids. Dr. Skau replied, it is about  $18^\circ$  for sterculic. I don't know what it is for malvalic. Dr. Harwood stated, I think it is published. There is probably a minimum point for a eutectic mixture. Dr. Frampton said, it is  $19^\circ$  for sterculic and  $17^\circ$  for malvalic acid. Dr. Goldblatt stated, we have to separate them from the mixture. Any suggestions for concentrating the acid? Dr. Kadesch remarked, it is like separating oleic from cis 8 - 9 acid. Mr. Feuge said, according to one method of analysis we have 100% malvalic acid, and according to another method we have only obtained 80% purity in our concentration procedure. We need a few pounds of the malvalic acid. Dr. Kadesch asked, have you tried the urea complexing method? Mr. Feuge replied, we tried





complexing with urea in the early part of our work, but discontinued that approach since it wasn't successful. We went as far as we could by that method. Dr. Frampton has worked further with the urea complexing and can tell you about that. We got two peaks on our best material by GLC. After using the urea complexing procedure, we still got the two peaks by GLC. Dr. DeJarlais asked, how about liquid-liquid partition distribution? Mr. Feuge replied, we were trying to use the silver nitrate-silicic acid column technique, but this destroyed our material.

#### REVIEW OF RESEARCH ON PHYSIOLOGICAL ACTIVITY OF CYCLOPROPENE FATTY ACIDS

Dr. Vernon L. Frampton reviewed recent research on the physiological activity of cyclopropene fatty acids.

#### DISCUSSION

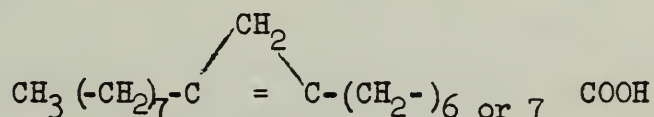
Dr. Goldblatt asked, is it the stearic/oleic acid ratio that is changed when cottonseed oils are fed? Dr. Frampton replied, in the liver, fat and brain tissue but not in the heart tissue. Dr. Kadesch remarked, it might be useful to use tagged malvalic acid and trace its fate in the animal. Dr. Frampton stated, if the Halphen Test is a test for cyclopropene ring, then we didn't have it in some of our samples, because some of the oils gave a negative Halphen acid response. We don't have the malvalic acid then. Dr. Goldblatt observed, maybe you have a derivative of it. Dr. Frampton stated, we are planning to repeat this experiment with the rats under stress conditions. We will try them on a treadmill. It is surprising why there is such a difference between liver fat from male and female rats.

#### DEVELOPMENT OF ANALYTICAL METHODS FOR CYCLOPROPENE ACIDS-- by E. L. SKAU

Dr. E. L. Skau reviewed research on the development of methods for the quantitative determination of cyclopropene acids. He described a method for the determination of cyclopropene fatty acids in refined and crude cottonseed oils to within 0.01% and another slightly less precise colorimetric method based on the Halphen color test.

#### DISCUSSION

Dr. Goldblatt asked, what size samples were involved there? Dr. Skau replied, 6 grams for low concentrations. We use from 0.2 to 6 grams depending upon the cyclopropenoid concentration. Dr. Kadesch asked, what is the chemistry of the reaction of HBr with C.P.A.? Dr. Skau replied (using the black-board) that the formula for the cyclopropenoid acids is



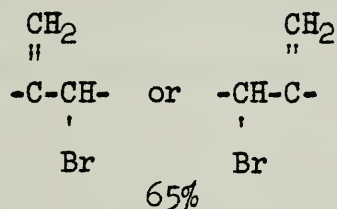
Sterculic acid has 7 C's on each side and malvalic 7 on one side and 6 on the other side of the ring. When HBr is added, the reaction is similar to



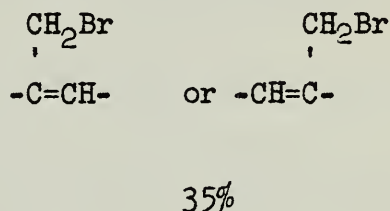


Rinehart's mechanism for the polymerization of sterculic acid. There are two possible forms, with a possibility of 4 isomers. If the parallelism with polymerization is complete, the reaction product contains about 65% of Form I and about 35% of Form II.

Form I:



Form II:



The HBr adds at a one-to-one ratio. The presence of Form II is shown by the Br peak in the IR spectrum. The iodine value of the oil is not changed, there is still one double bond. Dr. Kadesch asked, you mean it stops at one mole? Dr. Skau replied, yes, under the conditions of our reaction and titration. The 5.5 band disappears and you get the 11.06 band in IR. Dr. Kadesch asked, is sterculic acid optically active? Dr. Skau replied, I don't know. Dr. Kadesch remarked, I have a hunch it might be, although it might be almost indistinguishable from zero. Naturally occurring substituted acids usually are. Dr. Skau added, the paper on titration of sterculic acid and the epoxide of oleic acid is scheduled to appear shortly in the Journal of the Am. Oil Chemists' Society.

Dr. Kadesch asked, what is the relative speed of opening up the cyclopropene ring vs. epoxide ring? Dr. Skau replied that opening the cyclopropene ring is slower than opening the epoxide. The epoxide can be titrated nicely at 3° C. When the temperature is raised to 55°, additional acid is required to reach the end point. This takes about 2 hours at room temperature. But if you raise the temperature to 55° this titration can be done much faster. If you do the titration of sterculic above 60°, you begin to lose HBr. At 50° or 60° you get the same values. The GLC data doesn't agree with our results. I just don't believe the GLC.

Dr. Goldblatt asked, have you tried the 80% material, and then diluted it with corn oil and tested the mixture and can you then account for all of it? Dr. Skau replied, not with the 80% material. We did this, however, starting with a 50% mixture, namely *Sterculia foetida* oil. The observed and calculated values agreed. Dr. Goldblatt remarked, then, if you have the supposedly 100% pure material according to GLC, and you dilute it by 1/2, you get back less than 50% by GLC? Dr. Skau replied, we worked with HBr titration; we have not checked dilution method by GLC.

Dr. Kadesch asked, at 55°, will HBr react with linoleic acid? Dr. Skau replied, no. Dr. Kadesch asked, does it react with conjugated linoleic acid? Dr. Skau replied, we haven't tested that. I don't think it would. We have run safflower oil. We are interested in natural oils, but not in conjugated oils. Dr. Kadesch asked, would you have any conjugated linoleic present? Dr. Skau replied, no. Dr. Goldblatt asked, what about dimorphecholic acid containing oil? Mr. Magne replied, yes, we tried that. Titrated it at 3°; when the





temperature is raised the HBr splits off. Dr. Goldblatt asked, have you checked for any preformed conjugation? Dr. Skau replied, no. Dr. Dupuy said, I think you can get conjugation from C.P.A. by heat. Dr. Goldblatt remarked, I think we have two different lines of thought here and maybe you have a different question in mind. Dr. Kadesch said, I know alkali refining can produce a small amount of conjugation. Mr. Feuge replied, yes, that is so. Mr. Hoffpauir remarked, I think we can answer this suggestion by using tung oil. Dr. Skau replied, that would be the "acid" test. Dr. Goldblatt stated, good suggestion. Should be checked.

## REVIEW OF RESEARCH PROGRESS IN DEVELOPING FATTY AMIDE DERIVATIVES

Research progress in developing fatty amides was reviewed by Mr. Frank C. Magne. The objective of this research is to prepare, characterize, and evaluate chemically modified amides of fatty acids as plasticizers, stabilizers, polyurethane foams, and for other uses to further the industrial utilization of cottonseed and other domestic vegetable oils.

## DISCUSSION

Dr. Kadesch asked, how high a conversion to dimer acids was there? Mr. Magne replied, about 18%, Mr. Mod can tell you more exactly. Mr. R. R. Mod stated, overall conversion ranges from 15 to 30%. Dr. Kadesch stated that with autoclaving you should get about 50%, and without autoclaving you should be getting about 40%. Mr. Mod said that without autoclaving we could reach about 40% conversion, but the morpholide of such a material was still outside the compatible range.

Dr. Kadesch asked, if individual components were compatible, why wasn't the mixture compatible? Mr. Magne replied that this was the case in our material. Dr. Kadesch remarked, maybe the dimer was hurting you. What about Emery's dimer? Mr. Magne replied, Emery's dimer had good compatibility by itself. Dimer acids do not hurt. Dr. Skau stated that Emery's dimer had good properties as a morpholide. Dr. Kadesch asked, is there a significant difference between compatibility of oleic morpholide and linoleic morpholide? Mr. Magne replied, yes, a significant difference. Dr. Kadesch remarked that the dimer should eliminate the linoleic. Mr. Magne said that mixtures of oleic, linoleic and palmitic can tolerate as much as 22% linoleic acid and retain compatibility. We had hoped to get that reduction but we didn't reduce the linoleic down to 22% by dimerization. Dr. Kadesch remarked, maybe iso-thermal dimerization would have been better. With clay dimerization the linoleic and oleic are converted to about the same extent. A thermal dimerization would have given a better selective conversion of linoleic and left the oleic as it was. Dr. Skau said, that sounds like a better approach and it should be tried.

Dr. Kadesch asked, would you go so far as to say that all these piperidides could be primary plasticizers? Mr. Magne replied, yes, only they exhibit somewhat poorer thermal stabilities than the morpholides. This would furnish a use for such byproducts of industry; in addition, many of these piperidides have a broad spectrum of antimycotic activity. Dr. Kadesch remarked, that is good; but when you have used up all the source of byproduct in making another commercial product, to find more sources of that byproduct may prove costly. Mr. Magne agreed, yes, you're right there.





Dr. Kadesch asked, is that Empol 1024 on your slide? Mr. Magne replied, it is Empol 1014. Dr. Kadesch inquired, what about diesteramide? Have you considered other chain lengths? Mr. Magne replied that compatibility was improved but volatility adversely affected. Dr. Kadesch asked, what about 8N8 plasticizer? Mr. Magne replied that to get compatibility we have to doctor up the mixtures more. The 8N8 plasticizer, diesteramide, was good. The iminoacetic acid esteramide was compatible. Dr. Kadesch asked, have you compared the amides of diethylamine or dibutylpropylene? Mr. Magne remarked, perhaps we should have been looking at diethylamine instead of these; however, we are planning to study some of the higher N-dialkylamides.

Mr. Magne stated that we are interested in potential cheap sources of amines. Dr. Kadesch asked, secondary amines? Mr. Magne replied, yes, secondary amines. Dr. Fisher asked, any inexpensive method for making alkylated imide from primary amine? Simple aliphatic amines should be inexpensive. Dr. Kadesch replied, think general secondary amines are as cheap as you can find. Think Sharples has been making the cheapest for years by basic reactions. Have you tried aromatic amines? Mr. Magne replied, we tried them but they were incompatible. Dr. Kadesch asked, what about N-methyl aniline? Mr. Magne replied, the aromatic amines were light sensitive. We tried di-cyclohexyl and di-benzyl. The products were allowed to stand in the window. A shadow effect of object developed in the product, showing it was light sensitive. Dr. Kadesch remarked, I think the presence of unreacted amine or use of an impure amine was the cause of your trouble. I don't think the product itself would be light sensitive. Mr. Magne replied, that may be true. We have looked at several. Maybe we should look at this again for any unreacted amine or impurities.

Dr. Kadesch said that the price of secondary amines at the present situation may lead you to a search for a cheaper amine. Dr. Fisher remarked, I grant you that ammonia is more expensive than water. But the chemical industry is large and big enough to be able to make a cheaper secondary amine, and I think it could be done. Particularly, when making it on a large scale. Dr. Kadesch stated that morpholine is made on a large scale. I think diethanolamine is about the cheapest made on largest scale. Dr. Fisher asked, then the industry has to wait until the competition gets bigger?

Dr. Kadesch stated, if your method is dependent on piperidine, this is costly to synthesize. Alkyl pyridines would have to be synthesized in large quantities and those are more costly to get. Mr. Magne asked, are there any suggestions as to how to improve thermal stability? Dr. Kadesch replied, that is a bugaboo all along. Are you speaking of pigmented formulations? Mr. Magne said, no, in pigmented formulations the stability of our materials is as good as DOP. I am talking about unpigmented formulations. We are working with clear formulations. Dr. Skau remarked that 8N8 was not bad, since it was stable in formulations.

Dr. Fisher said, I think secondary amines are selling for about \$0.20 per pound. By producing them in sufficient quantity this should bring down the price. DOP was selling for 28 cents per pound when we first started this work, and the price of DOP now is 15 cents per pound. Dr. Kadesch added, your





materials do not have to be used straight. They can be used blended with DOP. This means opening the door to secondary plasticizers. The manufacturers like to split up the market, and use mainly mixtures. Phenol is selling for less than 15 cents per pound. Phenyl oleate and phenyl cellosolve oleate are some of these being used and competing. Dr. Fisher asked, what about isopropyl amine? From acetone - can't you make it now? Dr. Kadesch said, I was thinking about the use of a blend and not a specialty plasticizer. The low temperature plasticizers used alone are only being used for specialty purposes. For example, dibutylsebacate as plasticizer for butyl rubber is used alone, but the market for these is not too great. Dioctylsebacate and dioctylazelate are used alone as low temperature plasticizers in special cases and they are expensive. Dr. Fisher asked, then the emphasis would be more on making a blend or a single plasticizer which is inexpensive than on worrying about thermal stability? Dr. Kadesch remarked, the low temperature plasticizers are good but expensive. Adipate esters came on the market and made it easier to reach volatility limits. Have you considered your products for use in paint removers and in cosmetics? Dr. Goldblatt asked, what would be the requirements for a paint remover plasticizer? Dr. Kadesch replied, it is a combination of high solvent power and relatively low volatility. I am thinking about the castor oil products. The patent literature has a lot of work done but much of it was done with expensive things.

#### REVIEW OF RESEARCH ON THE DEVELOPMENT OF FIRE-RETARDANT COATINGS USING TUNG OIL ALKYDS

Dr. Harold P. Dupuy reviewed research on the development of fire-retardant coatings using tung oil alkyds. The objective of this research is to develop exterior and interior, intumescent, fire retardant coatings based on tung oil and tung oil derivatives, with other domestic oils, fatty acids, and chemical intermediates, such as polybasic acids, polyols, polyaminotriazines, isocyanates, carbonates, halogenated, and phosphorylated compounds as adjuncts.

#### DISCUSSION

Dr. Dupuy asked the group if anyone knew of any fire-retarding tests which would be more informative. There was no response. Dr. Kadesch asked, do you rely on pigmentation for fire retardancy? Dr. Dupuy replied, yes, and other additives, and modification of the vehicles. Dr. Kadesch asked, how does it compare with coating loaded with  $\text{Sb}_2\text{O}_3$ ? Dr. Dupuy replied, fire resistant but not fire retardant as it would not build up any carbonaceous mass. Dr. DeJarlais (NU) asked, do you also use it on a combustible base? Or is it for non-combustible ones? Dr. Dupuy replied, you can use it on a non-combustible base. Without fire retardancy it would blister; then rip off coating and allow the flame to burn the base. The coating I am working with is aimed at a combustible substrate but it can be used on metals. Dr. Goldblatt said, the paint looks good. Many firms are interested in such coatings for decorative purposes and fire-retardant properties.

Dr. Dupuy asked, do you know of any halogenated, phosphorylated, etc. compounds or oils being used for fire retardancy? Dr. Kadesch replied, I think Swift is offering a brominated oil. Mr. Hoffpauir remarked, it is used as an additive to an orange drink for cloud, I think. Mr. Feuge said that you need a





reactive group like a carboxyl group to tie it in to the oil. Incidentally, the iodine value of the brominated oil is zero. Dr. Kadesch stated that Victor company has lots of P-compounds on their shelf. Some of these are being used in fire-retardant coatings. Dr. Dupuy said, we're familiar with the phosphorus polyols. We know the percentage of phosphorus in the materials. Dr. Kadesch said, those phosphorylated polyols are being used for fireproofing in the polyurethane field. Dr. Dupuy remarked, we get a lot of information from visitors about the compounds available on the market, and a lot of visitors who come to the laboratory have expressed interest in making fire retardant their products such as foams, plastics, etc., anything almost.

Dr. McBee said, I can't understand why the high degree of secrecy around a project of this type. Dr. Dupuy said, I cannot discuss formulation because of the restrictions the Army has put on our laboratory work. Dr. McBee noted, this seems like a hindrance for you. It handicaps you in talking with anyone. I could tell you about innumerable phosphorylated or brominated compounds and perhaps give you a couple of dozen. It handicaps me from talking to you. I did all of the work for the Army on brominated and fluorinated compounds and the Army didn't put such a restriction on me. Dr. Dupuy replied, we have to go according to the contract. I don't have all equipment for testing. It has to be arranged for by the Army and this takes time. So this is not just a developmental problem on making the proper coating but in waiting for the Army to arrange for its testing. Dr. Goldblatt remarked, Dr. Dupuy, I think it would be very appropriate for you to try to get together with Dr. McBee at the end of this session for a private discussion. You can indicate the approximate requirements for % Br, P, etc., or types of materials in which you are interested and he may be able to give you more information from that. Dr. McBee noted that many companies such as Monsanto, Celanese, DuPont, and Hooker are working the fire-retardant field, and their people should be able to help you. Dr. Dupuy asked, do you know of tests used by anyone working with coatings? Dr. McBee replied, I do not have a knowledge of testing equipment. I know all about the chemistry of the materials, I have worked only on their chemistry. Do you know of any paints which will pass the 25-ft. tunnel test? Dr. Goldblatt replied, there are some inferior paints which do, but not any exterior paints, as we work on, that I know of. Dr. Dupuy said, there is no correlation between tests. We have to formulate something and figure out the best ways to get full benefits of the tests we have available for the coatings.

#### REVIEW OF RESEARCH ON NEW CROP OILS AND THEIR FATTY ACIDS

Research on new crop oils and their fatty acids was reviewed by Mr. Raiford L. Holmes. The objective of this research is to investigate the preparation and properties of valuable compounds such as hydroxy acids, amino acids, amides, and polybasic acids from the prominent and unusual acids in the oils from the seed of potential new oilseed plants such as Limnanthes and Cuphea, having production potentials as replacement crops indicated by the new crops screening program.

#### DISCUSSION

During the discussion of Cuphea, Dr. Kadesch remarked that, as a laboratory preparation, it is quite common to dehydrobrominate the  $\alpha$ -Bromo acids with





quinoline without getting any side reactions. This would avoid substitution. Mr. Holmes replied, we tried that. Dr. Kadesch noted that some biological activity distinguishes between cis and trans isomers. You could gear dehydrobromination to get maximum yield of either cis or trans form. Mr. Holmes replied, we haven't found that out as yet. Are there any suggestions for other work which can be done on decanoic acid. Dr. Kadesch replied, there are other rather cheap ways of making acids in this carbon number range. The availability of the C 8, C 9, or C 10 acids was somewhat limited. But with their preparation from  $\alpha$ -olefins by the petroleum industry now, there is a tremendous competitive problem to be dealt with. Dr. Goldblatt asked, do you know of any evaluations of the C 8, C 9, and C 10 esters as lubricants? Dr. Kadesch replied, they have been evaluated. Dr. Goldblatt asked, do you know whether one is better than another? Dr. Kadesch replied, I don't know. Mr. Holmes said that there is a lot of information about their usages as lubricants in the published literature.

During the discussion of the Umbelliferae, Dr. Kadesch asked are you referring to distillation of laurylaldehyde and adipic half aldehyde? The half aldehydes are notorious for forming non-volatile residues during distillation. In ozonization of oleic acid, steam distillation at atmospheric pressure is used for steaming out the pelargonic aldehyde. The azalaic half aldehyde can be obtained from the residue remaining after steam distillation. Mr. Feuge noted that it may distill at deodorization pressures. Dr. Kadesch said, well, good yields might be hard to separate by distillation. Dr. Swern in his early days did a lot of work on the preparation and separation of half aldehydes, and as I recall, he had a lot of trouble with them. For the general problem I would be leery of distilling procedures. For a better method, the separation by crystallization of bisulfite adducts might be preferable. Dr. DeJarlais asked, have you considered making the acetals to give more stable products? Mr. Holmes replied, no, we hadn't. We have now on our desk a manuscript from the Northern Laboratory dealing with separation of half aldehydes, their precipitation and purification. Dr. Goldblatt inquired, are there any more suggestions or questions? Dr. Kadesch remarked, I would suggest you ask the New Crops People for an oil which has a double bond in the 12, 14, 16 or some higher position. (General laughter from audience.)

During the discussion of Limnanthes douglasii, Dr. Kadesch said, for reacting this 70% perchloric acid with 5-eicosenoic acid, the best results gave an 80% yield of lactone. I assume it was purified 5-eicosenoic acid, and the yield was 80%, or did you say 85%? Mr. Holmes replied, yes, the acid was purified, and the yield was 85%. Dr. Kadesch remarked, then in the raw material for making the dimer, the double bond position doesn't matter much. Petroselinic was the same as oleic. Was p-toluenesulfonic acid a close second to perchloric acid for gamma-lactonization? Miss Sara Fore replied, yes, about 65% versus 80% yield. On the first recyclization, the yield was 90%, but it was not as pure. Dr. Kadesch asked, was that under the best conditions? Miss Fore replied, yes, the best temperature conditions used. Do you think a two carbon chain length from oleic acid would cause a difference in properties? Dr. Kadesch replied, probably it would not be of much significant difference. With only a 10% difference in carbon length,





you shouldn't expect much difference. For petroselinic acid versus oleic acid, with relation to dimer, the double bond position doesn't matter much, not really better or worse than oleic, and not better than C 20 acid. With the C 40 dimer, you might have different properties probably. The dimer to trimer ratio could be different. This is an important fact to be considered in some applications. I would check on that. Dr. Goldblatt asked, do you think there is a definite interest in oils of this type? Dr. Kadesch replied, synthetically, everything in Limnanthes douglasii is convertible to dimer. Mr. Holmes remarked, of course, all depend upon commercialization of crops of this type.

#### FAT EMULSIONS FOR INTRAVENOUS ALIMENTATION

Mr. Sidney Singleton reviewed research, supported by the Office of the Surgeon General, on the development of emulsifiable oils and fats for use in fat emulsions for intravenous alimentation.

#### DISCUSSION

Dr. Goldblatt asked, is the Swedish Emulsion supposed to be a good one? Mr. Singleton replied, their claims say it is good. The Army was interested in it, and wanted it prepared in sufficient quantity for testing. It has not been tested in this country on humans. Dr. Goldblatt asked, is that crude or purified egg phosphatide? Mr. Singleton replied, it is mainly phosphatidyl choline, prepared according to the Swedish procedure. Dr. Goldblatt asked, and there is inositol in the Swedish formulation? Mr. Singleton replied, yes. We did have some in ours before we purified our materials. But none developed in our SU formula as a result of processing. The Swedish sample contained inositol, so it must have been there from the time of preparation. Dr. Harwood asked, is pyrogenicity still a problem? Mr. Singleton replied, no. Dr. Goldblatt asked, Sidney, would you hazard a guess as to which is the best? The one which wets the glass or the one which doesn't wet the glass, that is, the SU non-phosphatide formula or the Swedish formula? Mr. Singleton replied, each has its drawbacks. The SU formulation, which wets the glass, on prolonged profusion causes pigmented livers in subjects receiving it. They find small brown granules distributed throughout the liver. The Swedish formulation which doesn't wet the glass, contains phosphatidyl material. It causes swelling between the liver cells. I can't say which condition is more desirable, the pigmentation or the swelling of the livers.

Dr. Kadesch asked, you said the pyrogenic problem was a thing of the past? Mr. Singleton replied, yes. Dr. Kadesch asked, it was shown to be connected with the emulsifiers added? Mr. Singleton replied, yes, and with the oils. In regard to this association of development of fever from infusions, in our present formulations, we only run into a few cases of fever every now and then. It is not a major problem like it was in the early days when we first started working on these emulsions. Dr. Kadesch stated, in previous visits, Dr. Goldblatt and I often talked of the Army wanting an emulsion whose fat composition was like the fat of the human body. Is that still true?





Mr. Singleton said, no, they have gotten away from that idea now. They will be able to use any emulsion so long as it is harmless and does supply caloric value. It is the caloric value they are interested in. Dr. Goldblatt remarked that with a synthetic fat, you could make it according to the composition of the body fat and also free of trace contaminants and you would not have any extraneous problem there. The problem is that we are trying to use our vegetable oils and have to use them with their formulation. It is the oil for which we are trying to find uses. The type of fat for use is not important; it is in getting a good product. Mr. Feuge asked, isn't one of the major problems with the emulsions the fact that they extract portions of the protein from the blood serum? Mr. Singleton replied, no, that isn't a major problem any longer. Mr. Singleton noted that the Upjohn emulsion has a 14-dosage lifetime limit on it. It can only be given 14 times during anyone's life period. The Army wants a product which can be used repeatedly on a subject without having to worry about such a limit. The effect of the SU formulation on production of liver pigmentation is being investigated. The Army is very interested in it because it looks promising as an emulsion which may be able to be given over a long period of time without any detrimental effects.

#### A MYOTONIC FACTOR IN PEANUTS

Dr. Vernon L. Frampton discussed a myotonic factor which has been found in peanuts. This research is part of a study of the relationships between those constituents of raw peanuts which contribute to improvement of processed peanut products and the intensity of such factors as aroma, texture, flavor, color, and physiological activity in the edible products.

#### DISCUSSION

Dr. Harwood asked, how stable is the material? Dr. Frampton replied, it is very hygroscopic. It is sensitive to acid and base. Dr. Harwood asked, does it contain nitrogen? Dr. Frampton replied, no, I don't think so. We haven't found any. Dr. Goldblatt asked, have you had carbon and hydrogen run on crude product? Dr. Frampton replied yes, the ratio's like that of a carbohydrate. The molecular weight is 250. With this hemostatic factor, we have changed the life of the hemophiliacs. Dr. Boudreaux of Louisiana State University (who will present a paper shortly in Copenhagen about this work) suffered very badly of hemophilia.

Dr. DeJarlais asked, how much do they have to eat? Dr. Frampton replied, Dr. Boudreaux eats about a pound of peanuts a day. Mrs. Louise Lee stated,





we received a request from a small boy in New Orleans, and were supplying him with 20 grams of extract per day. That would be equivalent to about one-half pound of flour per day.

Dr. Kadesch asked, how many hemophiliacs are there in the country?

Dr. Frampton said, there are 4000 registered hemophiliacs registered in the National Hemophiliac Society. I would say there are about 20,000 in the country. Mr. Holmes said that the Reader's Digest had an article in it about hemophiliacs. Mr. Persell remarked, you should read the article that just came out in the Saturday Evening Post. I think the article lists a much larger number. Mr. Dollear said, if I can recall correctly, the number in the country is more like 100,000 people.

Dr. Kadesch remarked, I should think a pharmaceutical company would be glad to take up this work and put it on the market. Dr. Frampton replied, I have contacted them and they are not interested. They say there just isn't enough money in it for them to think about such a product on a commercial basis. The number of hemophiliacs in the country is not large enough. Dr. Kadesch remarked, I doubt very much that all would turn down such a product. Which ones did you contact? Dr. Frampton replied, they are not interested in working with this type of product since there is no money in it. Dr. McBee asked, isn't it more appropriate for an academic laboratory to be interested in the identification of the myotonic factor because of the prestige to be gained by identification? Dr. Frampton replied, the drug companies have not shown any interest in it when we contacted them. Dr. Kadesch asked, those people who turned you down. Were those people of pharmaceutical companies strongly interested in blood disorders? Dr. Frampton replied, they indicated to us no interest.

Dr. McBee asked, is it still a problem of concentration? Have you reached maximum concentration? Dr. Frampton replied, by the old procedures we were using, yes, we had reached maximum concentration. Now we have a combination procedure, isolation by column and then paper chromatography. Probably we can increase concentration. It is still a problem of concentration. Dr. McBee asked, by continuous chromatography you are not able to increase concentration? Dr. Frampton replied, in previous schemes, we lost activity of the material. When it was chromatographed two times on paper, activity was lost. So we are going to go back to the column for further concentrating, and then separate it one time by paper chromatograms.

Dr. McBee asked, have moderate chemical reactions been able to reduce activity of derivatives to zero? Dr. Frampton replied, in dilute aqueous sodium bicarbonate or dilute acetic acid, the activity is lost by opening the lactone ring. Dr. Harwood asked, can activity be regained? Dr. Frampton replied, no. Dr. Kadesch asked, you are thinking of the lactone ring opening and closing as indicative of activity? Were you thinking of the aqueous sodium bicarbonate as opening up the ring? At what temperature did you do this? Dr. Frampton replied, it was done at room temperature conditions, and in aqueous solution activity was lost. Dr. Kadesch remarked, I doubt that the lactone ring would probably not open under room temperature conditions in that reaction. Dr. Frampton said, you should get some opening of the ring with the bicarbonate at room temperature.





Dr. Goldblatt asked, is the myotonic factor titratable? Dr. Frampton replied, that has not been tried. It is a good suggestion to be tried.

### THE COTTONSEED OIL COLOR PROBLEM

Dr. Vernon L. Frampton reviewed research on the cottonseed oil color problem. The objective of this research is to gain information on the chemistry of the problem pigments in off-colored cottonseed oils, on the chemistry of their formation, and to develop practical means for their estimation and elimination as a basis for upgrading low quality oils.

### DISCUSSION

Dr. DeJarlais asked, does the presence or absence of oxygen affect the rate of pigment formation in the oil? Dr. Frampton replied, no, not very much. Dr. Goldblatt asked, does anhydrogossypol form rapidly in esters? Dr. Frampton stated, the observed formation of anhydrogossypol in esters is most rapid and in some other solvents it is slower. Dr. DeJarlais asked, do the dark pigments of the oil come from the anhydrogossypol and not from the gossypol? Dr. Frampton replied, they are formed as a result of anhydrogossypol and not as a result of gossypol. Dr. Kadesch asked, why this pigment? The high acid strength chelates between high phenolic OH group with the aldehyde group of the solvent. Dr. Frampton said, yes.

Dr. DeJarlais asked, have you characterized or isolated pigment from oil? Dr. Frampton replied, no, not from oil. Dr. McBee asked, does the anhydrogossypol form in absence of air? Dr. Frampton said, I don't know. Dr. McBee asked, does it form in absence of oxygen? Dr. Frampton replied, you're talking about absence of molecular oxygen. Yes, it can form. Dr. Kadesch remarked, then the solution would be to avoid formation of anhydrogossypol or remove it when it is formed. Where does it occur? At what step of processing? Dr. Frampton replied, it is formed during storage of crude oils. It is a problem for processors who cannot immediately refine their processed oils. If the oils are refined immediately, there is no problem. Dr. Kadesch asked, is there a tendency for gossypol in a salt form to go over to dark colored pigments? Mr. Feuge replied, the Southern Laboratory did some work with addition of para-aminobenzoic acid to form addition compounds which could be removed from the oil and produce light colored oils.

Dr. Kadesch asked, if the gossypol can be removed immediately by alkali-refining, why don't the processors add a little NaOH to their oils during storage to prevent conversion to dark pigments? Dr. Frampton replied, I don't think that has ever been tried. Mr. Dollear stated, isn't it true that sodium gossypolate gives very dark, brown colored products in solution. I think Mrs. Berardi has worked with sodium gossypolate and can tell you that. I don't think that would be practical. Mrs. Berardi said, yes, sodium gossypolate in alkaline solution is very unstable and converts to many dark colored products. Dr. Frampton remarked, the problem is due to the method of extraction of the oil from the seed. The development of gland-free cottonseed should eliminate gossypol problems.





Dr. Goldblatt stated, the problem with the oils containing gossypol is how to prevent the conversion of this pigment to dark-colored products which cannot be removed by conventional alkali-refining and bleaching. Dr. DeJarlais asked, would an antioxidant prevent this conversion? Mr. Hoffpauir stated gossypol itself is an excellent antioxidant. It is about on equal par with tocopherol, and cottonseed contains a synergistic antioxidant activity from the tocopherol and the gossypol.

#### RESPONSES TO LAST YEAR'S RECOMMENDATIONS OF SU ADVISERS

Mr. Frank G. Dollear then reviewed the actions that had been taken by the Division in response to last year's recommendations of the Division Advisers. He said that Dr. Enos had suggested the use of activated clay catalysis for esterification in our work on new polyester fats. We gave this suggestion consideration but found that such catalysts acted at too high a temperature for our work.

Mr. Lovegren and Miss Gros have explained the esterification conditions required for preparing 1-monoglycerides and 1,2-diglycerides and studied conditions suggested by Dr. Harwood. As described by Miss Gros, mixtures of glycerides (using modifications of methods of Barrett, Devries, and Padley of Unilever ) have been analyzed by TLC, GLC and paper chromatography. There had been some discussion by Dr. Sparks regarding markets for polyester materials and that they should have a great commercial usage. One industrial firm has expressed definite interest in amylose esters.

With regard to fatty acid amides, Dr. Enos discussed possible usages as lubricating agents and anti-sticking agents, for use with polyethylenes. In a conversation we had with Dr. Rowland of U.S.I., he thought this market for fatty chemicals was rather limited. Rowland predicted only about 100,000 pounds of such materials could be utilized for polyethylene blocking agents as, for example, stearamide or similar compounds. Dr. Kadesch remarked, I thought the figure was larger than that. Maybe they have found out that they can use less additives, and that is why he quoted a smaller figure. Dr. Goldblatt asked, what percent was involved? Dr. Kadesch replied, when the additives totaled about 0.1%, that would have furnished a market for over 1 million pounds. That figure is much larger than the 100,000 lbs. you mentioned. Now, if they have found that they get by with adding a smaller amount of those materials, then the amount required would be smaller. If the amount of additives are now down to about 0.01%, this would account for your figure of 100,000 pounds. Of course, more would be used for film form than for bulk form such as the molded adhesives. Mr. Dollear said, I recall, in a recent C & E News, a figure of 300,000 to 400,000 pounds market potential for antioxidants and UV screening agents for polypropylene. We sent samples of amides to U.S. Industrial Chemicals for evaluations. They showed no advantage over oleoamide and stearamide. Dr. Kadesch asked, what did they evaluate? Mr. Magne replied, the piperidide of oleic acid was sent. Of course, that was a liquid sample. The lubricating characteristics and blocking properties may differ, dependent upon whether the sample is in liquid or solid form. We sent Visking solid samples, and have never received any word about their performance.





Dr. Enos remarked, I have talked to Dr. Skau about your samples. I planned to evaluate them in our laboratories, but found out later they would not be screened. I did not request samples because they would have remained on our shelves. At that time other problems became more important and the situation has not changed since then.

Dr. Kadesch stated, I think about 0.1% oleamide and stearamide are being used for films as anti-slip agents and lubricants. I think the chemical industries would be happy to try new sources of such agents. One of the major used fatty materials is calcium stearate, which functions as a neutralizer.

Mr. Dollear asked, how much additives are put in? Dr. Enos replied, the total amount of additives may be in range of 5%. They include materials for: anti-static, anti-lubricant, lubricant, anti-fungal, UV screening, peroxide destroying, free radical inhibiting, and anti-oxidant activities.

Mr. Dollear asked, would your people be interested in making tests on some of these compounds? Dr. Enos replied, that is questionable. The industry is more interested in trying a combination and also a combined activity of additives in order to cut out some they are already using. Then the question is, where could you get one tested by itself when the industry is using combinations.

Mr. Dollear said, I suppose we could get someone to test the materials under contract work. Do you think it would be worthwhile? Do you think the potential is big enough for us to undertake contract testing? Dr. Enos replied, it might be worthwhile, but is questionable, besides, you would have to find a place which could evaluate them properly, and I don't know of any. Also, industry is trying to combine functions to reduce number of additives. Dr. Goldblatt asked, what are anti-static agents? Dr. Enos replied they are polyamines or amides. Mr. Hoffpauir asked, how do they work? Dr. Enos replied, they bleed the charge off the surface. They can be applied by spraying, by surface coating or by applying internally. Mr. Dollear said, there is some theory that they migrate to the surface and act there to bleed off the charge.

Mr. Dollear said, Dr. Sparks made a suggestion to look at the use of possible applications of copolymers of vinyl phosphonates with tung oil vehicles rather than Diels Alder adducting it with tung oil. We're working in this area, but not on that specific reaction. We are trying to retain the drying oil properties of the oil and at the same time put the phosphorus in the drying oil vehicle. Mr. Dollear stated, Dr. Harwood had commented on petroselinic amine in connection with possible application as a corrosion inhibitor. The double bond closer to the carboxyl could be better.

Dr. Harwood replied, I don't think I said that. The duo-amine type of Armour is better than a straight amine. Mr. Dollear said, that is what you suggested. We have now made a corresponding "duoamine" from petroselinic acid but have not yet evaluated this compound. With regard to amide plasticizers, Dr. Sparks suggested substituted formamides. Magne has reported working on this. He told about making dimethyl formamides having excellent plasticizer properties but volatility was a problem.





In the separation of fatty acids of Limnanthes douglasii, Mr. Dollear reported that Dr. Reaville suggested the use of thiourea. After consulting the literature, it was apparent that the openings in the thiourea were too large. We might have used cyclohexyl ester in that work and formed a clathrate with thiourea. However, thiourea might be a good bet to try with the cyclopropene acids. Dr. Harwood suggested high temperature distillation. In attempts to distill at high temperatures we got some isomerization to the trans form. At 300° there was some isomerization, and this may have been due to the sulfur which is in the Limnanthes meal.

Dr. Kadesch noted that in normal commercial methods they will get a little of the oleic going to the trans form. You're certain to get some of it going to the trans form. Mr. Dollear asked, that is with heat? Dr. Kadesch replied, yes.

Mr. Dollear continued, Dr. Reaville had suggested the need for a water resistant starch. Mr. Holmes told you about his work on starch modified with decanoic acid as an adhesive. Regarding the suggestion of testing decanoic acid esters as lubricants, it has been learned that the Standard Oil Co. has already done such work.

Dr. Enos suggested talking to Procter & Gamble Co. about dimethyl lauryl amine oxide. We have not yet checked on this. The Cuphea species right now as an industrial crop does not look too promising as a source of capric acid. Dr. Kadesch remarked, I should not think the Standard Oil Company would be interested in evaluation of capric esters as lubricants. Their pelargonic acid finding was an incentive for them to find a use for it. They are geared to pelargonic acid and must find uses. I thought the pelargonic acid was similar to coconut toppings. Dr. Enos said, I heard a talk by a fellow (from NU) at the American Oil Chemists' Society meeting (paper No. A-4). He reported about a new oil with C 12 acid that was similar to coconut oil that Procter & Gamble is using. For their work on detergents, they are using the amine oxide to get high cleaning power. If they ever announce it as bio-degradable, the whole chemical industry will follow them. Dr. Kadesch remarked, I understand P & G are cooperating with Cargill in this work. Dr. Enos said, they are making the amine oxide through alcohols, with an excess capacity for alcoholysis.

#### REVIEW OF TECHNICAL ASPECTS OF OILSEED CROPS AND NAVAL STORES RESEARCH PROPOSALS

Mr. Carroll L. Hoffpauir, Assistant Director for Program Development, briefly reviewed the research proposal system of the Division. He stated that the importance and need for submitting research proposals cannot be overemphasized. The Southern Division is responsible for sound research leading to the increased utilization of the commodities assigned to it. Proposals for projects are essential to sound and systematic planning for such research and form the basis for recommendations by the Advisory Committees. Information required in a research proposal includes:

- |                              |                               |
|------------------------------|-------------------------------|
| 1. Title                     | 4. Plan of Work               |
| 2. Objective                 | 5. Estimate of Funds Required |
| 3. Problem and Need for Work | 6. References                 |





Problems for agricultural research are presented by many individuals. They originate from many sources, both within and without the Department. It is a job of the scientists to develop research proposals designed to solve these problems. Each proposal is evaluated at several levels within the Department. To determine appropriate action, numerous factors are considered at each point of review. These factors are similar at all organizational levels, although the importance given to particular factors may be quite different.

The major points for consideration in evaluating research proposals are:

- I. Importance of the problem that the proposal is designed to solve.
- II. Competence of the research organization and staff.
- III. Relationship of the proposal to other research.
- IV. Soundness and feasibility of the research plan.

In the application of these criteria, it is assumed that proposed projects are within the legal authority of the organization which is to carry them out, that the relative merits of various proposals will be considered in light of the cost of conducting each, and in light of the availability or probable availability of funds.



Report of the Oilseed and Naval Stores  
Advisers to the Director

on  
May 1, 1963

Dr. Fisher welcomed the advisers, and asked for their comments and suggestions on SU's oilseeds and naval stores research programs.

Naval Stores Program

Dr. DeJarlais (NU) thought the naval stores research had great promise, particularly since a low-cost material was involved. However, he felt that perhaps an outside (industry) viewpoint was needed.

Dr. Harwood stated that naval stores research was a remote area to him, but he felt it was an interesting type of chemistry and should not fail to produce something interesting and good. He thought SU had a good program.

Dr. Enos said he had been aware of the program for some time. It is a well organized program and there is a keen awareness of the problems involved. In his estimation the fundamental work of naval stores - - research on new components, isolation of new compounds - - is one of the most important functions. This work should be continued. He was disturbed about the research on photo-oxidized acids - - i.e., these compounds not behaving as peroxides. The nature of the products should be proved. Perhaps polarographic methods might be applicable here. He thought the turpentine work, and also the work on pinene oxides, had good potential. The glycol series of compounds should be studied. Preparation of polyurethanes from turpentine, for applications such as the foamed-in-place type in ship hulls, should be investigated. Johns-Manville and Armstrong Cork would be interested in such products, especially if fire resistant. Phosphorus compounds (2 or 3% in the final polyurethane product) could probably be used to achieve this.

Dr. Kadesch was impressed with the great variety of things going on in the research, and thought the program was good. He felt it might be of interest to place more stress on simple isomerization to put double bonds in other positions, thereby producing certain unsaturated compounds having more value than the turpentine starting material. Dr. McBee thought that if the new hydrocarbons were made available cheaply, they could be chlorinated to obtain products with insecticidal value. Mr. Lawrence pointed out that the Naval Stores Laboratory hasn't gone into this, but Hercules has covered the field pretty well.

Dr. Goldblatt asked whether the chlorinated camphenes had been investigated by Hercules. Dr. Enos replied in the affirmative. He stated that chlorinated pinene was covered by a Hercules patent. At one time Goodrich sold this product but in view of the patent coverage, has been discouraged from doing so.





In reply to a question by Mr. Lawrence as to whether any good products were to be made from allo-ocimene, Dr. Enos said it is a very discouraging prospect. Hercules and a number of others have tried with no success. Dr. Fisher suggested trying the Diels-Alder reaction. The raw materials employed for this reaction are getting cheaper now.

### Vegetable Oil Program

Dr. Kadesch thought the program, in general, was well conceived and executed. It would be wise for SU to deemphasize plasticizers in his estimation. There might be an illusion of success, but the price of DOP is 15 1/2 cents per pound. A new approach to obtain something out of the ordinary would perhaps be all right. SU should determine basic properties of the materials as Armour did years ago, rather than strive to find where the products will find commercial use. Industry and others will look at the data and suggest possible uses. SU should not go too deeply into a particular end use. Dr. Fisher asked Dr. Kadesch if he meant more emphasis on preparing pure compounds and determining their properties, including systematic studies of physical properties as related to structure. Dr. Kadesch replied in the affirmative.

In continuing the discussion, Dr. Kadesch pointed out that the antibacterial activity of decanoic acid was one lead, but many other uses were excluded. SU should make many new derivatives of decanoic acid and let others find uses for them. Dr. Fisher noted that Dr. Goldblatt had just recently become Chief of Oilseed Crops Laboratory and would review work just beginning and make proper changes. In the case of EU's work on epoxidation, they did basic work first; others exploited the findings, and a good stabilizer for PVC resulted. He felt that SU should guide the fundamental work into areas that might find practical applications. Dr. Kadesch said SU could do the best job on fundamental work, and industry the best job on applications. SU should wait for a period of time and see if industry picks up a development before going further with it.

Dr. Kadesch thought it would be difficult to justify cost in the case of petroselinic acid. Lauric and adipic acids are presently readily attained commercially by other means. Cleavage products not readily available or attained should be sought. Dr. Fisher felt the half aldehyde-acid would not be readily available. Dr. Kadesch agreed. However, he pointed out that Emery Industries could go into preparation of these aldehydes by ozonolysis of oleic acid if they desired to do so.

Dr. Fisher stressed the fact that uses peculiar to the new crops material must be found. SU must try to direct its research in this direction. Dr. Kadesch thought two points were important: (1) development of cleavage products of petroselinic acid having new properties, and (2) obtaining a better knowledge of crops research aspects. The possible use of the half aldehyde-acid in Nylon 7 was proposed by Dr. Fisher. It could be reacted with HCN, reduced to the amine, and water cut out to obtain the omega-amino acid for this application.





The polyfunctional derivatives are of greatest interest to industry, according to Dr. Kadesch. However, the markets for azelaic and pelargonic acids are actually not very large. The aldehydes are very versatile. Oils of longer-chain type, high in  $C_{20}$  (as, for example, oils from Limnantes), and the high erucic acid content oils, are good ones on which to work, rather than petroselinic acid. Dr. Fisher stated that NU's work on crambe, a high erucic acid oil, showed good promise. He pointed out, however, that the petroleum industry is coming out with primary alcohols now of which we need to take cognizance.

Dr. McBee apologized for his short stay due to unavoidable circumstances. He said he differed somewhat with Kadesch on his viewpoint. A lot of people are doing basic research, but he felt only about 10% of it was really good research. He was opposed to SU spending a lot of time on making new compounds, as its mission was to enhance utilization of crops. SU should take on the function of an industrial organization and find practical applications. Economics should be faced up to, and an approach made from the practical point of view. Basis research should be done, but we must look for practical applications. SU should make evaluations of what the materials are good for---not wait always for industry to do this. Dr. McBee suggested that SU bring in young academic professors versed in organic chemistry and the current literature to consult about the research. They could give seminars, and research problems could be posed to them. In this way, new ideas and reactions would be found and SU's researchers would be stimulated. The regular SU advisers are more valuable in advising about practicality of areas of work; young professors could help SU with specific technical problems. He stated he had twenty-five new phosphorus-halogen compounds which might be of interest in SU's program.

Dr. Fisher said SU does use this approach somewhat, mentioning Dr. Kosolapoff who advises us on phosphorus chemistry. Because of the recent change in regulations requiring short, definite appointments for consultants, it is more difficult for SU to do this now. He felt we must do both fundamental and applied research. The trend at SU is toward an increasing percentage of basic research; but practical applications are also necessary and desired by Congress. The advisers can help SU by: (1) keeping us informed of the problems and trends in industry, and (2) suggesting technical approaches to use in our research.

Dr. Enos was in general agreement on this. In industry there are chemists to conduct exploratory research and market development chemists to see that new applications are found. Later, sales development people take care of selling. This is done on an organized basis. SU should combine information from four or five companies as a basis for ascertaining where to go in its research. For example, several companies are now going into production of amine oxides---a 160,000,000 pound per year potential market. It would have been desirable for SU to know this a year or two ago. Mr. Persell agreed that there was a need for continuing contact with industry. Dr. McBee noted that a key group in industry is the product evaluation group, and SU needs such an industry contact group.





Dr. Goldblatt asked for comments concerning the tung oil research.

Dr. Kadesch said emphasis should be on synthesis of materials, methods to improve yields, and related research. Then industry could apply the findings more fully.

Dr. Enos said a conference on information exchange and retrieval within SU and among the ARS organizations might be useful. At the time some products are made there is no apparent use, but years later the product may be just the thing you are seeking for a new use. It is important to keep good records to find such things at a later date when needed.

Dr. Kadesch suggested that the conversion of amine oxides to amide oxides might be tried. An interesting series of compounds might result.

Dr. Harwood stated he was closer to Kadesch's than McBee's viewpoint. The product development people need to know the properties of the materials. SU should give industry new compounds and as many of their properties as possible. Although SU doesn't always know it at the time, industry finds the SU information valuable and useful; in these cases, industry just keeps it to themselves. Dr. Kadesch made the point that if SU hands industry a development which is too well developed, they will shy away from it. Industry wants to do some of the work on it, obtain patent protection, and the like.

With regard to the research on new crop oils, Dr. Harwood was of the opinion that the petroselinic acid and the decanoic acid work should not be emphasized. If you really want industry to develop interest in these new crop oils, C<sub>20</sub> type oils or derivatives should be made available to industry for investigation. He encouraged SU to continue its work on confectionery coatings. Mr. Hoffpauir asked if there was any good indication of the potential market for these coatings--there is disagreement among industry people about this. Some feel the current price of cocoa butter is a fictitious one, and if a synthetic product is introduced, the price of natural cocoa butter will come down. Dr. Harwood had no information to offer concerning this. Dr. Fisher suggested it might be possible to make the true flavor components of cocoa butter; Dr. Harwood agreed this might be possible.

Dr. Fisher asked if it would be possible to epoxidize, then make the hydroxy lactone from oleic acid. Dr. Harwood thought this could probably be done. Dr. Kadesch commented you could also dehydrate and open the ring.

Concerning the cyclopropene acid research, Dr. Harwood felt the chemistry was getting ahead of the toxicology. Dr. Fisher commented he had heard the opposite from others. Mr. Hoffpauir noted that a difference of one carbon atom may make a difference in physiological activity of these acids.





Dr. Kadesch favored obtaining a general knowledge of the acids by studies of their chemistry. Pure compounds, rather than oils, should be used for the research on physiological activity. He believed SU was perhaps going too far into the practical aspects. Mr. Hoffpauir pointed out the difficulty in synthesizing cyclopropene acids and the low yields obtained. The major problem is to get sizable quantities of the pure materials for determination of physiological properties. Dr. Kadesch stated that "synthetic" foods have the kiss of death. Only once in a great while will natural foods be banned. He cited many natural foods containing poisonous constituents.

Dr. Fisher asked the advisers' opinions about tung oil work, in view of its price of about 40 cents per pound. Dr. Goldblatt wondered if a stronger program on coatings was desirable. Dr. Enos did not know. He felt tung oil was a rather expensive chemical raw material. Dr. Kadesch believed improved growing and harvesting methods were needed to bring the price down to about 10 cents per pound. Dr. Goldblatt noted that the normal price is about 20 cents per pound. The current price is abnormally high, and will probably continue high for a while.

Dr. Enos stated that an abstract service was found to be good in his company. It is desirable to have good communications within and between laboratories at SU and also other ARS laboratories. In his organization the technical information service is applied to both the company and the open literature. There is complete separation of the company's proprietary information (reports, correspondence, patent applications, etc.) and the public literature (books, journals, patents, etc.) to the point that the personnel and records are on different floors. The library service includes indexing, storage and circulation of books and journals and patents. There are translation, abstracting, and reviewing services. In the case of open literature, the information is typed on special multilith paper (legal size sheets which are perforated and tear into eight 3-1/2 x 5 sheets) and circulated to chemists, indexed, and filed. There is information retrieval on both the open literature and company literature using coding and IBM machines. He believed it important that the internally generated literature at SU be brought to the attention of all those at SU who should know about it. At Hercules, the research chemists write three-month progress reports. These are abstracted and put on card file and in the information retrieval system. This helps tremendously. Dr. Kadesch pointed out that a professional searcher or literature reviewer frequently picks up information the research worker might miss. Dr. Enos agreed.

Mr. Hoffpauir asked what size staff is required for such an operation. Dr. Enos estimated that at Hercules one Ph.D. research chemist (supervisor), three part-time translators, and about three B.S. chemists for literature work were used in the operation. Certain parts of the information are transferred to the IBM information retrieval system---for example, to correlate the structure of compounds with uses. Dr. Fisher felt it would be desirable to make a study to determine the level (%) of effort used on this information retrieval program.





## ACKNOWLEDGMENT

Appreciation is expressed to Mrs. Leah Berardi and other members of the Oilseed Crops Laboratory and to the various members of the Naval Stores Laboratory who contributed to the program and assisted in reporting the meeting.



UNITED STATES DEPARTMENT OF AGRICULTURE  
AGRICULTURAL RESEARCH SERVICE  
SOUTHERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION

PROGRAM FOR CONFERENCE

OF

ADVISERS ON OILSEEDS AND NAVAL STORES

GENERAL CHAIRMAN

R. M. Persell  
Assistant Director, SU

Monday, April 29, 1963 - 9:00 a.m.  
Naval Stores Station  
Olustee, Florida

R. V. Lawrence  
Chief  
Naval Stores  
Laboratory, SU  
Presiding

9:00 a.m.      Introductory Remarks

R. V. Lawrence  
Chief, NSL, SU

9:10 a.m.      Review of research on pine gum  
composition, oxidation of resin  
acids, esters from pine gum deriv-  
atives, and exploratory photochemical  
reactions of pine gum derivatives

R. V. Lawrence  
and Staff of  
Pine Gum  
Investigations  
NSL, SU

10:20 a.m.      Review of research on rosin modifications,  
terpene acids, pinene oxide, isolation  
of levopimaric acid, and analysis of  
resin acid mixtures rich in levopimaric  
acid

G. W. Hedrick  
and Staff of  
Rosin Investi-  
gations, NSL,  
SU

11:30 a.m.      Review of research on turpentine  
condensation and oxidation reactions

G. S. Fisher  
and Staff of  
Turpentine  
Investigations  
NSL, SU

1:00 p.m.      Lunch

2:30 p.m.      Tour of laboratories and discussions  
with individual chemists

6:00 p.m.      Leave Lake City for New Orleans, Louisiana





Tuesday, April 30, 1963 - 10:00 a.m.  
Auditorium, Third Floor  
Southern Regional Research Laboratory  
New Orleans, Louisiana

R. M. Persell  
Assistant Director, SU  
Presiding

10:00 a.m. Welcome

C. H. Fisher  
Director, SU

10:05 a.m. Oilseed Crops research of SU

L. A. Goldblatt  
Chief, OCL, SU

10:20 a.m. Review of research on confectionery fats

N. V. Lovegren  
OCL, SU

10:55 a.m. Review of research on new polyester fats

Audrey T. Gros  
OCL, SU

11:30 a.m. Review of research on cyclopropene fatty acids in cottonseed oil isolation and inactivation

R. O. Feuge  
OCL, SU

12:00 noon Review of research on physiological activity of cyclopropene fatty acids

V. L. Frampton  
OCL, SU

12:30 p.m. Lunch

1:30 p.m. Development of analytical methods for cyclopropene acids

E. L. Skau  
OCL, SU

2:00 p.m. Review of research progress in developing fatty amide derivatives

F. C. Magne  
OCL, SU

2:45 p.m. Review of research on the development of fire-retardant coatings using tung oil alkyds

H. P. Dupuy  
OCL, SU

3:05 p.m. Intermission

3:30 p.m. Review of research on new crop oils and their fatty acids

R. L. Holmes  
OCL, SU

4:00 p.m. Fat emulsions for intravenous alimentation

W. S. Singleton  
OCL, SU

Wednesday, May 1, 1963 - 9:00 a.m.  
Auditorium, Third Floor

R. M. Persell  
Assistant Director, SU  
Presiding

9:00 a.m. A myotonic factor in peanuts

V. L. Frampton  
OCL, SU





9:10 a.m.	The cottonseed oil color problem	<u>V. L. Frampton</u> OCL, SU
9:20 a.m.	Response to last year's recommendations of SU advisers	<u>F. G. Dollear</u> OCL, SU
10:00 a.m.	Intermission	
10:30 a.m.	Review of technical aspects of oilseed crops and naval stores research proposals	<u>C. L. Hoffpauir</u> Assistant Director, SU Program Development
12:00 noon	Lunch	
Director's Office - 1:00 p.m. Room 2004		
1:00 p.m.	Report of Oilseed and Naval Stores Advisers to Director	
Departure from SRRL		



UNITED STATES DEPARTMENT OF AGRICULTURE  
AGRICULTURAL RESEARCH SERVICE  
SOUTHERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION

CONFERENCE OF ADVISERS ON OILSEEDS AND NAVAL STORES

April 29, 30 and May 1, 1963

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